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Analytical and Sampling Methodology for Characterization of Polynuclear Aromatic Compounds in Indoor Air

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ANALYTICAL AND SAMPLING METHODOLOGY FOR CHARACTERIZATION OF POLYNUCLEAR AROMATIC COMPOUNDS IN INDOOR AIR

by

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Table IV. PAH concentrations in air in study home A.

Compound	Concentration - ng/m^3			
	Kitchen	Living Room	Bedroom	Outdoors
Quinoline	1.02	1.34	1.14	0.21
Isoquinoline	0.87	1.02	0.90	0.18
Phenanthrene	49.25	72.02	58.99	35.44
Anthracene	2.67	3.67	2.31	4.20
Fluoranthene	13.00	22.54	12.06	18.35
Pyrene	6.18	11.17	5.28	13.11
Cyclopenta(c,d)pyrene	0.69	0.52	0.65	3.74
Benz(a)anthracene	0.69	0.67	0.55	2.69
Chrysene	1.37	1.42	0.92	3.92
Benzofluoranthenes	1.75	1.82	0.93	4.91
Benzo(e)pyrene	1.03	0.98	0.73	2.88
Benzo(a)pyrene	0.94	1.07	0.76	2.85
Indeno(1,2,3-c,d)pyrene	0.89	0.83	0.68	2.47
Benzo(g,h,i)perylene	1.75	1.40	1.41	5.10
Coronene	1.67	1.00	1.22	3.60

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16. ABSTRACT

Sampling and analysis methodology were developed for the collection and quantification of polynuclear aromatic hydrocarbons, their nitro derivatives, and their nitrogen heterocyclic analogs in indoor air. The methodology was evaluated in a study of air in ten homes. The study included homes with and without woodburning fireplaces, gas heat and appliances, and smoking occupants, and with a range of ventilation rates. The range of concentrations in the homes and factors that systematically contribute to those concentrations of selected polynuclear aromatic compounds were estimated. Some practical limitations on the sampling equipment and methodology were identified.

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ABSTRACT

Sampling and analysis methodology were developed for the collection and quantification of polynuclear aromatic hydrocarbons, their nitro derivatives, and their nitrogen heterocyclic analogs in indoor air. The methodology was evaluated in a study of air in ten homes. The study included homes with and without woodburning fireplaces, gas heat and appliances, and smoking occupants, and with a range of ventilation rates. The range of concentrations in the homes and factors that systematically contribute to those concentrations of selected polynuclear aromatic compounds were estimated. Some practical limitations on the sampling equipment and methodology were identified.

Polynuclear aromatic hydrocarbons (PAHs) and nitro-substituted polynuclear aromatic hydrocarbons (NO_2-PAHs) have been identified in organic extracts of ambient air particulate matter.[1-5] Many of the identified PAHs and NO_2-PAHs are potent carcinogens, mutagens, or both.[2-6] Therefore, it is important to determine PAH and NO_2-PAH levels in ambient and indoor air as part of the characterization of air quality.

The objectives of this pilot project were to develop, evaluate, and test sampling and analysis methodology for PAHs and NO_2-PAHs in ambient and indoor air; to determine the ranges of PAH concentrations in residential air; and to estimate the influence of smoking, wood-burning fireplaces, gas or electric utilities, and ambient air intrusion on these concentrations. The results of the pilot project are intended for use in the planning and design of a future more extensive study of indoor air quality. In this paper, the sampling and analysis phases of the pilot project are discussed, and their implications for the larger study design are indicated.

Pilot Project Design

Eight study homes and two background homes were selected for this project. The homes were chosen to include homes with and without smoking occupants, with and without wood-burning fireplaces in use, and with and without gas heat and appliances. All the gas-heated homes also had gas-fueled major appliances, including gas stoves for cooking. The background homes were all-electric homes with no smokers and no fireplaces. Figure 1 shows the matrix of home characteristics selected as stratification variables in this study. Choosing homes according to this matrix allowed the use of statistical analysis to provide estimates of the effects of the stratification variables on the PAH concentrations.

Several target PAH, NO_2-PAH, and heterocyclic PAH compounds were selected for this study. The compounds selected satisfied one or more of these criteria: occurrence of the compound in ambient air samples at significant concentrations; reported potential as a marker compound for overall PAH concentrations, emissions from mobile sources, tobacco smoke, or wood smoke; significant emissions from these sources; and known carcinogenicity or mutagenicity. Tables I and II list the target compounds.

Sampling

A modified EPA medium volume sampler with a rotary carbon vane oil-less vacuum pump was used in the indoor air sampling. The sampler was equipped with a quartz fiber filter and a polyurethane foam (PUF) adsorbent cartridge. The sampling head was mounted on a tripod to place the inlet 60 inches from the floor. A heavy-wall 1-in tube led through a window port from the sampling head to the pump, which was placed in a sound-insulated box just outside the house. Indoor samples were collected over consecutive 8-hr periods, at times and in locations chosen to correspond with the occupants' activities, as shown in Table III. The sampler flow rate was approximately 12.5 m^3/hr, which allowed collection of a sample of 100 m^3 of air in an 8-hr period.

During the indoor sampling, an outdoor 24-hr air sample was collected in the back yard of each study home. An EPA medium volume sampler, equipped with a quartz fiber filter, a PUF adsorbent cartridge, and a General Metals by-pass motor was used.

Air exchange data during the sampling periods were obtained by making an initial injection of SF_6, followed by sampling at one, three, five, seven, and eight hours with air-tight syringes.

Analysis

In a previous study, it was found that the PUF gave rise to large amounts of unknown compounds that interfered with the PAH analyses, even after extensive clean-up by Soxhlet extraction according to standard procedures.[8] Therefore a new clean-up procedure was developed, which was found to eliminate the interferences. The clean-up procedure involved sequential compression/decompression of the PUF plug in 800 ml each of toluene, acetone, and 5% ether/hexane. This was followed by Soxhlet extraction for 16 hr with acetone, and drying in a vacuum oven at room temperature. All PUF cartridges were cleaned by this technique before use.

A preliminary study was performed to determine how well PAH compounds are recovered from PUF cartridges, and to determine how well PAH compounds are retained on the PUF during eight hours of air sampling. Cleaned PUF cartridges were spiked with a mixture of the target PAHs and NO_2-PAHs. Two spiked cartridges were extracted and analyzed immediately. Two other spiked cartridges, plus a third with no spike, were used to sample ambient air for eight hours in the sampler described above. The three PUF cartridges were then removed, extracted, and analyzed. The results of these analyses are shown in Figure 2. The recoveries are shown in the figure in order of increasing molecular weight or number of rings. Most of the target compounds were efficiently recovered from PUF, with the exception of the two most volatile compounds, naphthalene and quinoline. Slightly poorer recovery of 1-nitropyrene from PUF also occurred, but this was not important, since later results showed that all the 1-nitropyrene in the real air samples occurred in the particulate fraction collected on the filter. During the sampling of air for eight hours, significant losses of PAH compounds with one, two, or three rings occurred. Less volatile PAHs with four or more rings, for example fluoranthene, pyrene, and larger molecules, were recovered completely from the PUF. An exception was cyclopenta(c,d)pyrene, which is highly reactive and presumably disappeared from the PUF by forming oxygenated or other derivatives.

After sampling, the filters and PUF plugs were Soxhlet-extracted for 16 hr with methylene chloride or 5% ether/hexane, for the filters and the PUF respectively. The extracts were concentrated and analyzed by chemical ionization gas chromatography/mass spectrometry (CI GC/MS), using positive chemical ionization for the PAH and heterocyclic compounds. Negative chemical ionization GC/MS was used to determine the NO_2-PAH compounds, since it has been demonstrated[9] to be more sensitive for these compounds, and the expected levels of the NO_2-PAHs were very low.[6,7]

Although high-performance liquid chromatography (HPLC) was considered for analyzing the samples in this study, it was found[9] that the sample extracts required extensive clean-up and fractionation before HPLC could be used. In contrast, the sample extracts required no clean-up or fractionation for the CI GC/MS analysis. Thus CI GC/MS turned out to be a more cost-effective analytical technique.

Results

One of the goals of this study was to find out whether a mass of material sufficient for both chemical analysis and bioassay could be collected indoors in a reasonable length of time without extensively perturbing the indoor environment with high-volume sampling. The more demanding requirement is that for bioassay. A standard Ames test generally requires about 12 mg of material. However, a new forward mutation-based microbioassay under development in these laboratories[10] requires only about 1 mg. The masses of particulate matter collected on the filters ranged from 1.3 to 38.7 mg indoors and from 3.0 to 22.7 mg outdoors. These particles yielded 0.4 to 28.9 mg and 0.4 to 8.7 mg of extractable organic material indoors and outdoors, respectively. Extractable organic material on the PUF cartridges ranged from 2.2 to 8.7 mg indoors and from 1.4 to 10.1 mg outdoors. Thus, although the samples on the low end do not yield sufficient material for bioassay, those in the mid to high end of the mass range certainly do. These higher mass samples are, in addition, the samples of intrinsically higher interest in terms of human exposure.

Distributions of the PAH compounds between the filter and the PUF were as follows: three-ring PAH, 90% on PUF; four-ring PAH, 80% on PUF; five-ring PAH, 10% on PUF; and six- and seven-ring PAH and NO_2-PAH, 100% on the filter. These distributions parallel, in general, the volatilities of the individual PAH compounds.

Concentrations of the individual target PAH compounds measured in homes ranged from 0.00 to 143.58 ng/m^3; phenanthrene was most abundant, with fluoranthene and pyrene second and third most abundant, respectively. The larger PAHs, which include such carcinogens as benzo(a)pyrene and indeno(1,2,3-c,d) pyrene, were present individually at concentrations from 0.00 to 7.35 ng/m^3. Data for two of the study homes are given in Tables IV and V. Home A, in Table IV, is a gas-heated home with no fireplace and no smoking occupants. Home F, in Table V, is a gas-heated home in which a fireplace was in use and the occupants smoked. The overall PAH concentrations are not only higher in Home F than in Home A, but also the quinoline concentration in Home F is very much higher than it is in Home A -- as much as 23 times higher in the living room! Because of the poor recoveries of quinoline from PUF, the concentrations of this compound reported here are probably low. Statistical analysis of the total data shows a significant correlation between quinoline concentration and smoking, at the >99% confidence level, but not between quinoline concentration and the other stratification variables: type of heating system/appliances and use or non-use of a woodburning fireplace. This is an important finding, since quinoline is a candidate for a marker compound to assess the contribution of tobacco smoking to overall indoor pollution.

Total four- to seven-ring PAH concentrations were generally highest in the homes occupied by smokers, with little effect of fireplace use, but a statistically significant increase with gas compared to electric heat and appliances. Concentrations of one- and two-ring PAHs were usually higher indoors, whereas the concentrations of five- to seven-ring PAHs were higher outdoors.

Nitro PAH concentrations were low, in the 2 to 185 pg/m^3 range[7]. No effects of smoking or fireplace use were observed on the 1-nitropyrene levels; however, this compound was present at greater concentrations in gas than in

electric homes. An important finding was the presence of 3-nitrofluoranthene (3-NF) at substantially higher levels than those of 1-nitropyrene (1-NP) in nearly all samples, both indoor and outdoor. Since 3-nitrofluoranthene is a potent mutagen, it should be monitored in future studies.

Statistical analyses of all the data gathered in this study were performed for each target compound. In addition to the stratification variables smoking, fireplace use, and type of heating system, other sources of variation were considered. These are: time of day, location within the residence, home-to-home variation, day-to-day variation, air exchange rates, and other non-systematic variation. Although the detailed results of the statistical analyses are not appropriate for discussion here, they do have implications for the design of large-scale indoor air quality surveys.

Location of the sampler in the home was a source of variation, significant at the 95% confidence level. Because cooking leads to large changes in PAH concentrations in the kitchen, and these changes appear to depend on what specifically is being cooked, kitchen sampling is less likely to give results representative of the overall home environment. Both living room and bedroom sampling locations were significant sources of variation of the PAH concentrations; however, living room concentrations were usually higher. Thus, the living room may be a better choice of sampling location to determine the extent of PAH exposure.

Home-to-home variation was larger than day-to-day variation. Thus repeat sampling in the same homes assumes less importance than sampling in several different homes.

The air exchange rates measured in this study varied from 0.2 to 0.7 exchanges per hour. Such exchange rates could affect the indoor PAH levels measured by as much as 5 to 10%. However, the air exchange rate was found to be statistically significant for the concentrations of only a few target compounds: benzofluoranthenes, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-c,d) pyrene, and benzo(g,h,i)perylene, For these compounds, the average effect of outside air intrusion is estimated to be about -0.4 ng/m^3 per exchange per hour.

Conclusions

This study showed that the sampling system was effective for most of the target compounds. It collected sufficient material for chemical analysis and for limited bioassay. Highly volatile or reactive PAH compounds were not retained by the sampling system; for these compounds, alternative adsorbents should be evaluated. A new clean-up procedure for PUF, compression rinsing, eliminates the interferences formerly encountered in PAH analyses of extracts from samples collected on PUF.

Both cigarette smoking and the presence of gas heat and appliances affected the PAH concentrations significantly. In contrast, the use of woodburning fireplaces was not a significant influence.

Although air exchange rates were inversely related to PAH levels, the effect was statistically significant for only a few compounds.

Of the nitro polynuclear aromatic compounds measured, 3-nitrofluoranthene was present both indoors and out in greater concentrations than was 1-nitropyrene. The indoor concentrations of 3-NF were correlated with smoking,

whereas the 1-NP concentrations were higher in homes with gas heat and appliances, but the significance of the correlation was low. Because of the greater amount of 3-NF and its greater mutagencity, future studies should include this nitroaromatic compound.

The compound quinoline may serve as a marker for the contribution of tobacco smoke to indoor PAH levels. However, further evaluation is necessary, with a sampling system that provides better recoveries for this compound than those obtained with polyurethane foam adsorbent.

Variations related to sampling location in the home and related to sampling in different homes of the same type are important, and should be considered in the design of more comprehensive indoor air studies.

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Table I. Target PAH compounds.

Compound	Reason for Selection
Phenanthrene	Marker for volatile PAH
Anthracene	Marker for volatile PAH
Fluoranthene	Marker for total PAH
Pyrene	Nitro derivatives strong mutagens
Benz(a)anthracene	Active mutagen, carcinogen
Chrysene	Weak mutagen, carcinogen
Cyclopenta(c,d)pyrene	Active mutagen, mobile source marker
Benzofluoranthenes (b,j, and k)	Active mutagens, carcinogens
Benzo(a)pyrene	Active mutagen, carcinogen, historically important
Benzo(e)pyrene	Weak mutagen
Indeno(1,2,3-c,d)pyrene	Carcinogen
Benzo(g,h,i)perylene	Mobile source marker
Coronene	Mobile source marker

Table II. Target nitro and heterocyclic PAH compounds.

Compound	Reason for Selection
1-Nitropyrene	Strong mutagen, mobile source
3-Nitrofluoranthene	Strong mutagen
Quinoline	Active mutagen, carcinogen, tobacco and coal combustion product
Isoquinoline	Isomer of quinoline

Table III. Sampling schedule.

Sampling Time	Location
0700-1500 hr	Kitchen
1500-2300 hr	Living room
2300-0700 hr	Bedroom

Table V. PAH concentrations in air in study home F.

Compound	Concentration - ng/m^3			
	Kitchen	Living Room	Bedroom	Outdoors
Quinoline	8.09	31.23	4.10	0.45
Isoquinoline	4.41	13.63	13.17	1.54
Phenanthrene	112.49	132.33	103.11	46.09
Anthracene	5.01	8.12	4.35	3.28
Fluoranthene	24.28	37.37	22.11	16.90
Pyrene	10.74	18.10	10.09	9.07
Cyclopenta(c,d)pyrene	0.52	0.35	0.00	0.55
Benz(a)anthracene	1.01	2.25	0.73	1.11
Chrysene	1.98	5.25	1.77	2.53
Benzofluoranthenes	2.69	5.83	1.68	3.37
Benzo(e)pyrene	1.92	3.12	1.00	1.85
Benzo(a)pyrene	1.57	3.33	0.73	1.70
Indeno(1,2,3-c,d)pyrene	1.18	2.58	0.81	1.07
Benzo(g,h,i)perylene	2.75	2.77	0.95	2.49
Coronene	3.08	0.91	0.30	1.26

List of Figures

Figure 1. Matrix of study home characteristics.

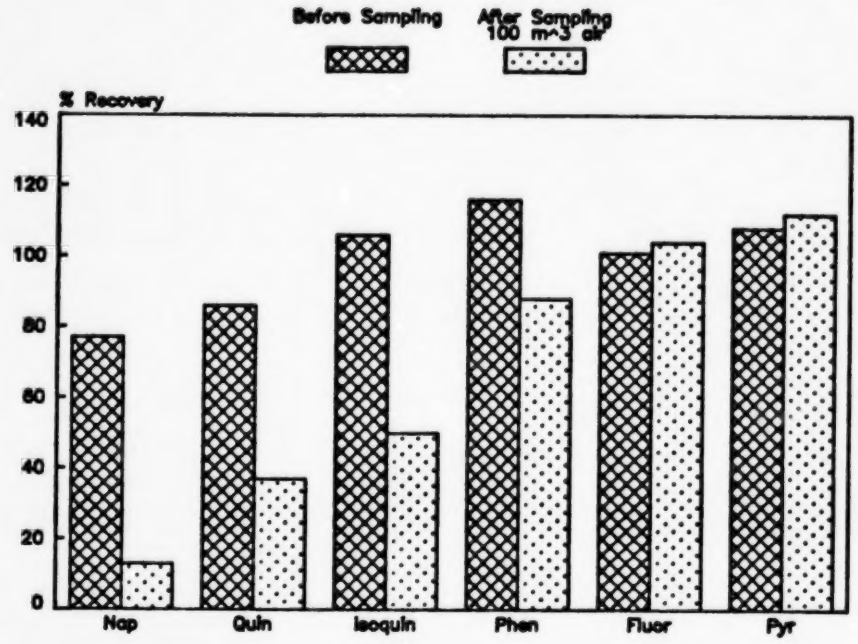
Figure 2. Recovery of PAH compounds from spiked PUF cartridges. Compounds are: Nap, naphthalene; Quin, quinoline; Isoquin, isoquinoline; Phen, phenanthrene; Fluor, fluoranthene; Pyr, pyrene; 1-Mepyr, 1-methylpyrene; Baa, benz(a)anthracene; 1-NO_2pyr, 1-nitropyrene; Ccdpyr, cyclopenta(c,d)pyrene; Bghiper, benzo(g,h,i)perylene; Cor, coronene

Study Homes

	Fireplace in use	Fireplace not in use
Smoking	D,F,F2	E,J
No smoking	B,C,C2	A,I

Background Homes

	Fireplace not in use
No smoking	G,H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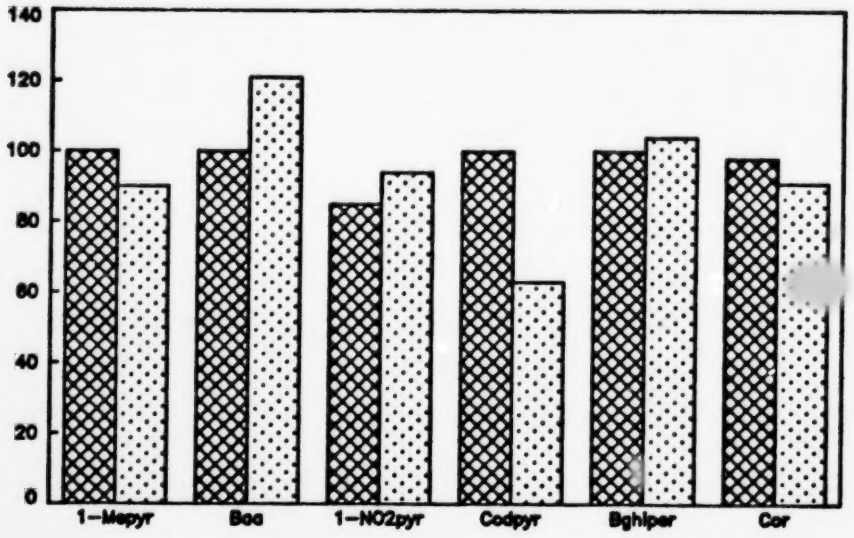
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